LA-UR-19-28184

Approved for public release; distribution is unlimited.

Title:	An Introduction to Quantum Dots as Scintillating -Radiation Detectors
Author(s):	Starvaggi, Nicholas Charles
Intended for:	Report
Issued:	2019-08-13

An Introduction to Quantum Dots as Scintillating γ-Radiation Detectors

Nicholas Charles Starvaggi
NEN-3: International Threat Reduction
Summer 2019 SULI Internship

Scintillation Technology

- A **scintillator** is any material capable of converting some of the energy of incoming incident particles into low-energy photons in the ultraviolet to visible range for a variety of technical applications. [1]
  - Nuclear engineering
  - Medical imaging
  - National Security
  - High-energy physics

- Scintillating Radiation Detectors
  - Inorganic or organic composition
  - Luminescent properties
    - Identify radioactive sources
    - Characterize radiation
  - Quantify radiation intensity

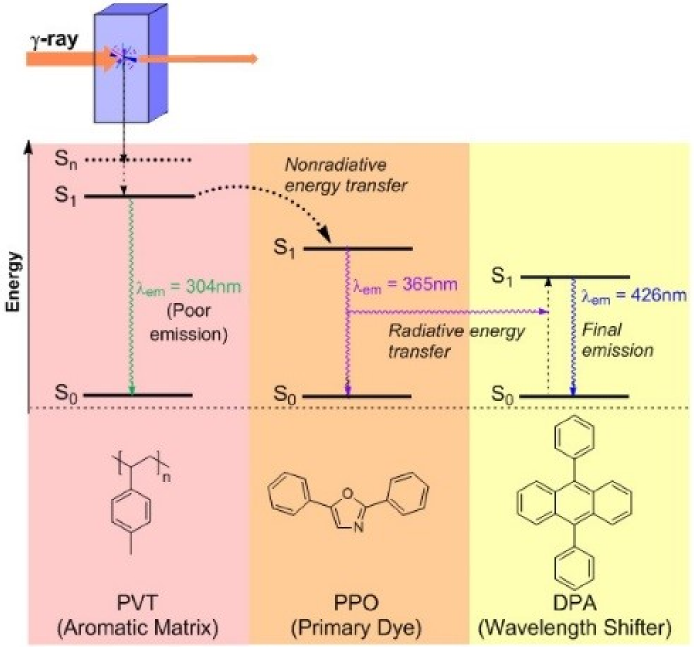

Fig. 1: *Mechanism for γ-radiation down-conversion with plastic scintillators.*[1]

Types of Scintillators

- Inorganic Crystals[1]
  - NaI(Tl), CsI(Na)
    - High light yields for γ-radiation detection and spectroscopy
    - Expensive and susceptible to rapid degradation

- Organic Materials[1]
  - Crystals
    - Acceptable light yields
    - Fragile, difficult to machine and polish
  - Liquids
    - Large-scale production possible
    - Flammability and toxicity of aromatic solvents
  - Plastics
    - Low light yields
    - Minimal hazards

Fig. 2: *NaI(Tl) scintillator. Courtesy of www.ost-photonics.com*

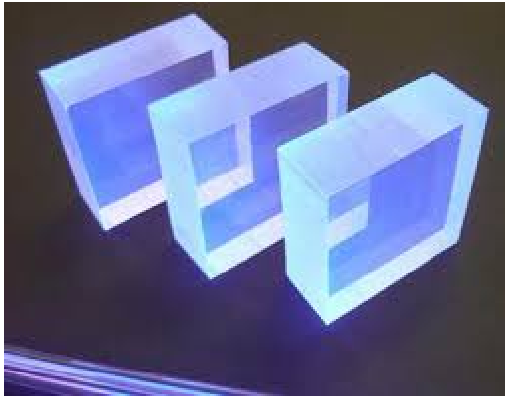

Fig. 3: *Luminescent plastic scintillators. Courtesy of www.oeaw.ac*

NaI(Tl) Scintillator Schematic

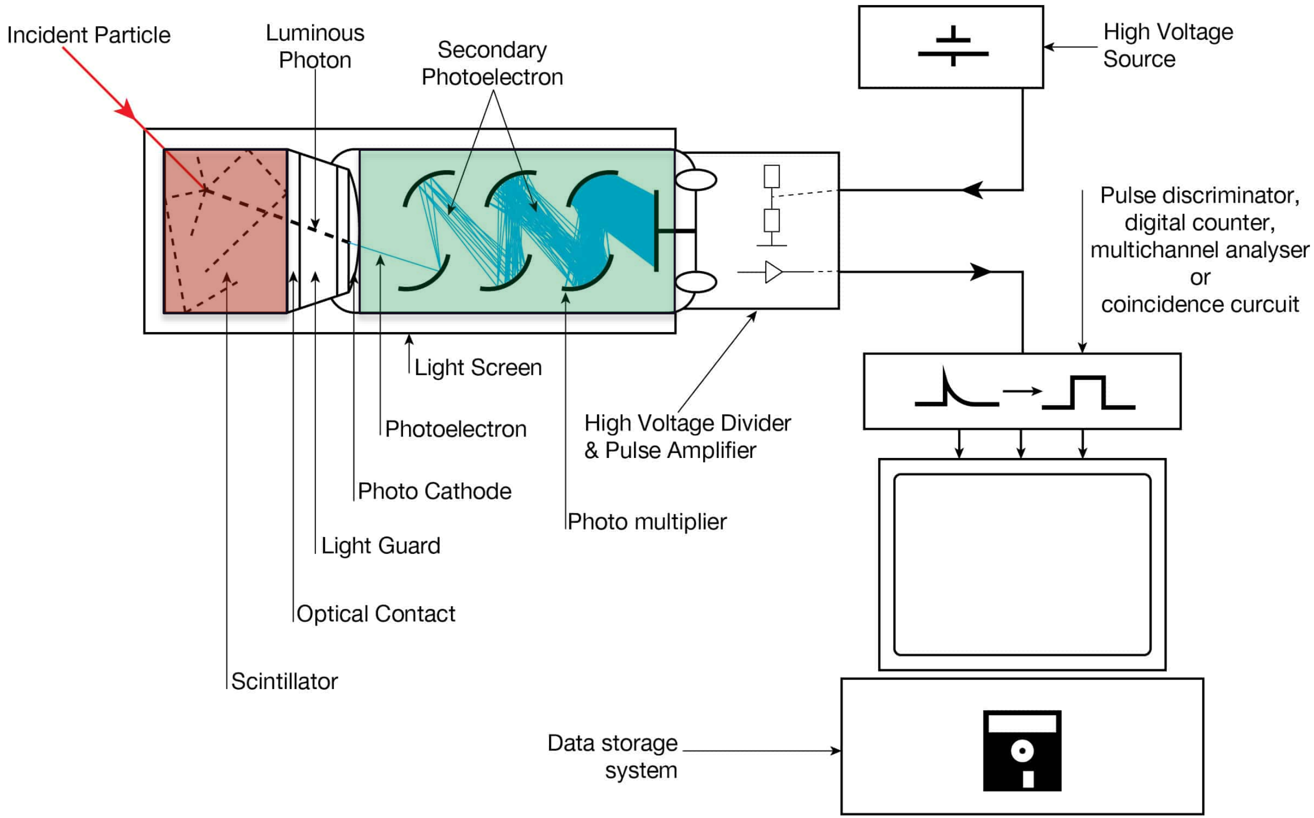

Fig. 4: *NaI(Tl) Scintillator and PMT schematic. Courtesy of www.nuclear-power.net*

Scintillating γ-Radiation Detectors

- Ideal Scintillator Characteristics[2]
  - High-Z composition
    - Increase γ-attenuation
    - Generate photoelectron production
  - High light yield
    - Increased photon count per unit of energy deposited
    - Optical clarity
  - Short emission decay lifetime
    - Timing resolution[4]
    - Immediate system response
  - Low Cost
  - Ease of large-scale fabrication

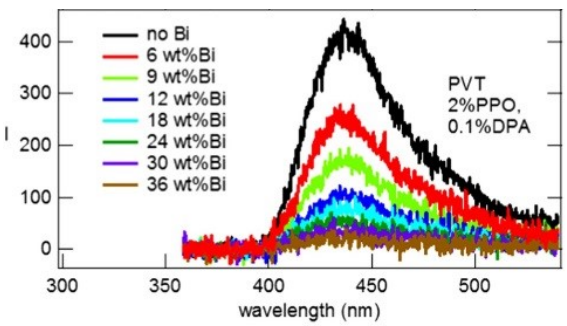

Fig. 5: *Effect of organo-bismuth (high-Z) loading on the radiation response of a scintillator.*[3]

Wavelength Shifters for Advanced Scintillators

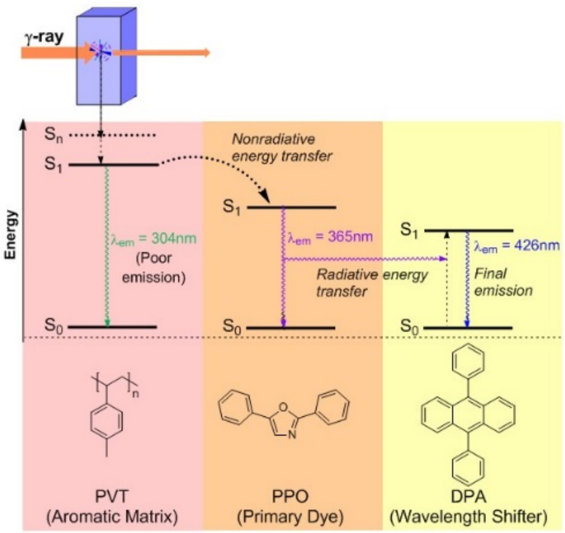

Fig. 6: *Mechanism for γ-radiation down-conversion with fluor-doped plastic scintillators.[1]*

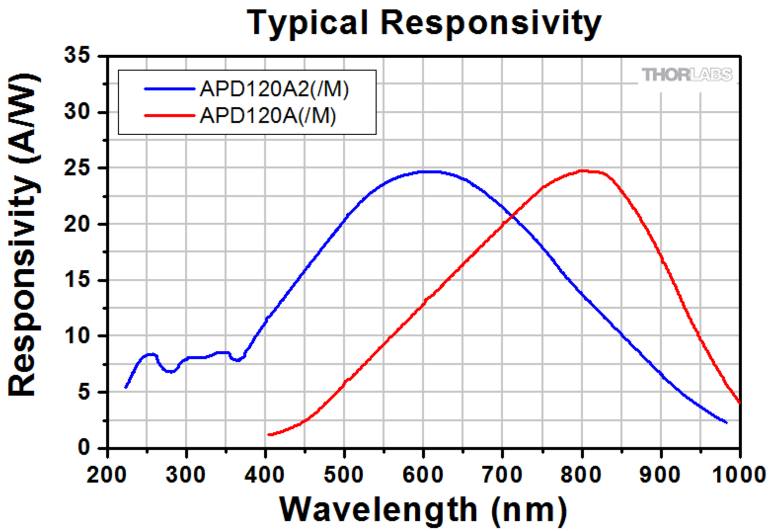

Fig. 7: *Typical responsivity (A/W) of an avalanche photodiode (APD). Courtesy of www.thorlabs.com.*

Quantum dots offer an alternate method to γ-radiation downconversion in the next generation of photomultiplication devices.

QD Basics

- Semiconductor Nanoparticle Crystals
  - Inorganic Core
    - High-Z element composition
    - Interactions with radiation
  - Ligand Shell
    - Easily manipulated
    - Determines solubility[5]
- Quantum Mechanical Properties
  - Particle size
    - 2-10 nm
  - Energy bandgap
  - Emission profile[6]

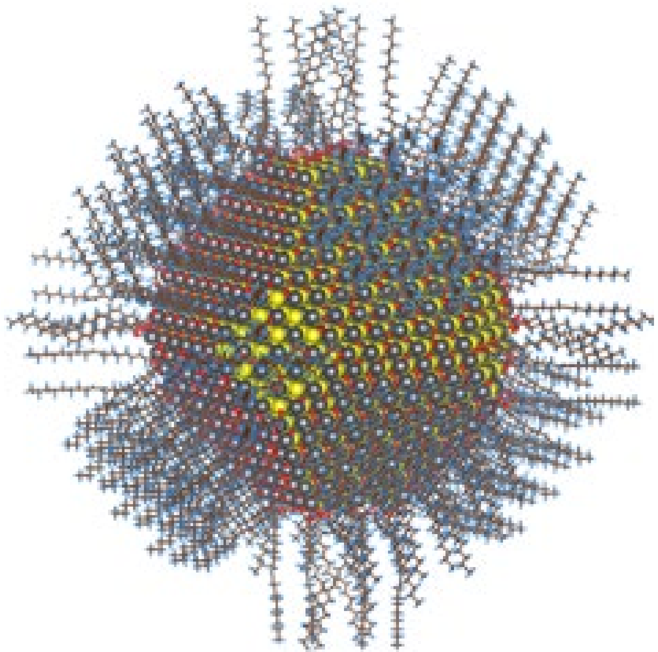

Fig. 8: *Ball-and-stick model of a QD showing the inorganic core and ligand shell. Fig. adapted from proposal.[6]*

Key Properties

- Characteristic Emission Color
  - Dependent on particle size and bandgap
- Smaller QDs, Larger Bandgap
  - More energy to promote a single e^- to an excited state
  - Results in a higher energy frequency (ν) and shorter wavelength (λ)
  - Emit light towards violet/indigo end of the visible light spectrum
- Larger QDs, Smaller Bandgap
  - Less energy to promote a single e^- to an excited state
  - Results in lower ν and longer λ
  - Emit light towards red/orange end of the visible light spectrum

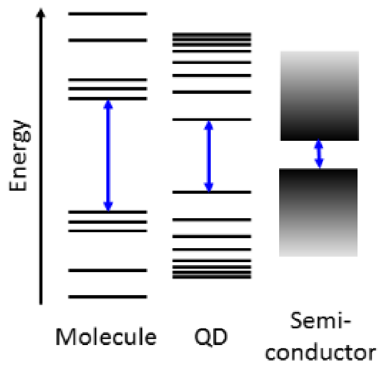

Fig. 9: *Comparison of the energy orbital diagrams of molecules, QDs, and semi-conductors.*

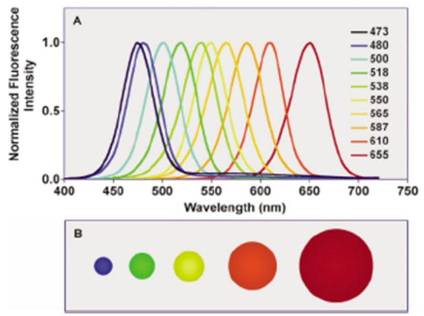

Fig. 10: *QD sizes displayed along the visible light spectrum.*[6]

Synthesis of QDs

- Basic Procedure
  - Pyrolysis (decomposition) of organometallic precursors in hot solvent generates QDs[5]
    - QDs are bound in aqueous solution
    - Subsequent reactions in coordinating solvents are often performed to manipulate the ligands
  - Reaction length affects nanoparticle size

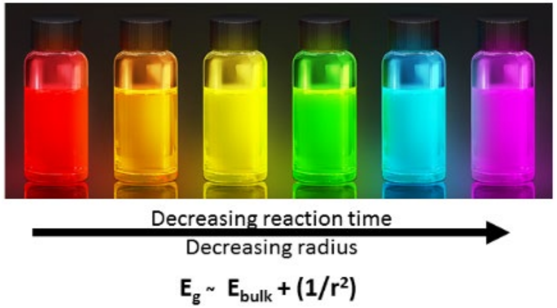

Fig. 11: *Effect of reaction time in the synthesis of QDs.*[6]

- Special Focus on High-Z Element Combinations
  - Cd/Se, Cd/S
  - Pb/Se, PbS
  - In/As, In/P
  - Zn/Se, Zn/S

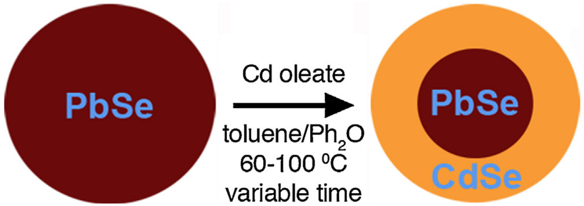

Fig. 12: *Diagram of a PbSe/CdSe core-shell quantum dot.*[7]

QDs as Scintillating γ-Radiation Detectors

- QD Research
  - Nanometer dimensions increases bandgap and allows for visible luminescence[9]
  - Integrates necessary high-Z inorganics with organic dyes in a polymer matrix[8]
    - Polystyrene (PS) and polyvinyl toluene (PVT)
    - Potential copolymerization applications with acrylate compounds to increase durability
  - Resulting plastic scintillator is low-cost and has a short-emission decay lifetime
    - Optical transparency contributes to high light yield

- Challenges
  - Self-attenuation (self-reabsorption)
  - Incorporation into a polymer matrix

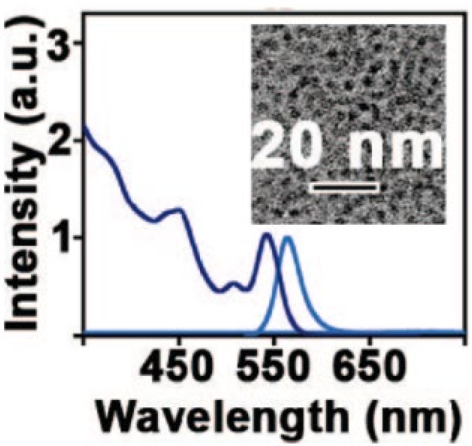

Fig. 13: *Self-attenuation in average quantum dots. Fig. adapted from proposal.*[6]

Giant Quantum Dots (gQDs) in LANL Scintillation Technology

- gQDs, developed by Jennifer Hollingsworth at CINT, are a LANL-patented alternative to standard QDs[10]
  - Ultra-thick CdSe/CdS core-shell system
  - Increased photostability

- Special Core-Shell Functions
  - Shell absorbs light, core emits light
  - Absorption energy is higher than emission energy
    - Shell serves as the wider-gap semiconductor in comparison to the core material
  - Light emitted by a single gQD is thus not reabsorbed by other gQDs in polymer matrix

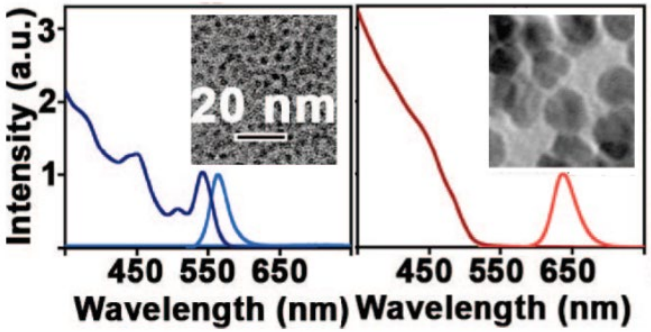

Fig. 14: *Comparison of standard QDs (left) and LANL-patented gQDs (right). The absorption (dark lines) and emission (light lines) demonstrate the lack of self-attenuation in gQDs. Fig. adapted from proposal.*[6]

Research Goals, Challenges, & Solutions

- Polymerization of PS and PVT
  - Initial photoinitiation via BAPO
  - Copolymerization with 2-carboxyethyl acrylate ($C_6H_8O_4$)
    - 3:1 Ratio
    - 6:1 Ratio
- Incorporate wavelength shifters
  - POPOP ($C_{24}H_{16}N_2O_2$)
  - Characterization
    - IR Spectroscopy
    - UV-VIS spectrophotometry
    - Fluorimetry

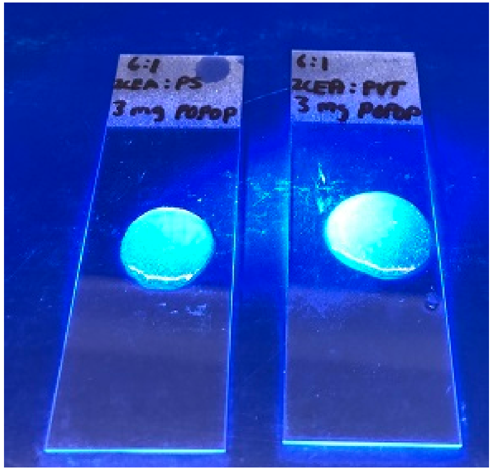

Fig. 15: *2CEA:PS/PVT (6:1) samples with 3 mg of POPOP exposed to UV light.*

Initial IR Results

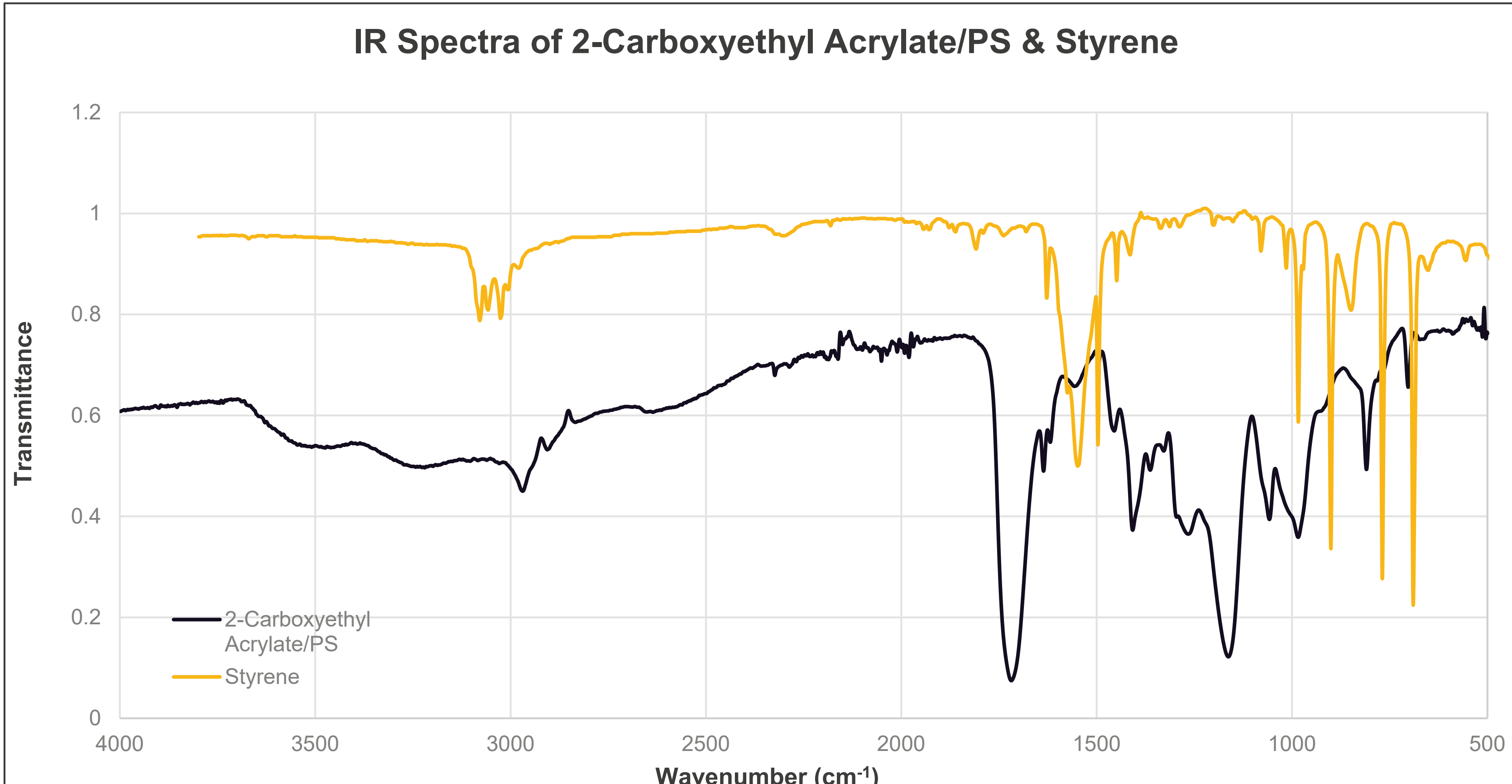

Fig. 16: *IR spectra of 2CEA/PS composite (black line) and neat styrene (orange line). Styrene IR courtesy of www.webbook.nist.gov.*

IR Results (cont.)

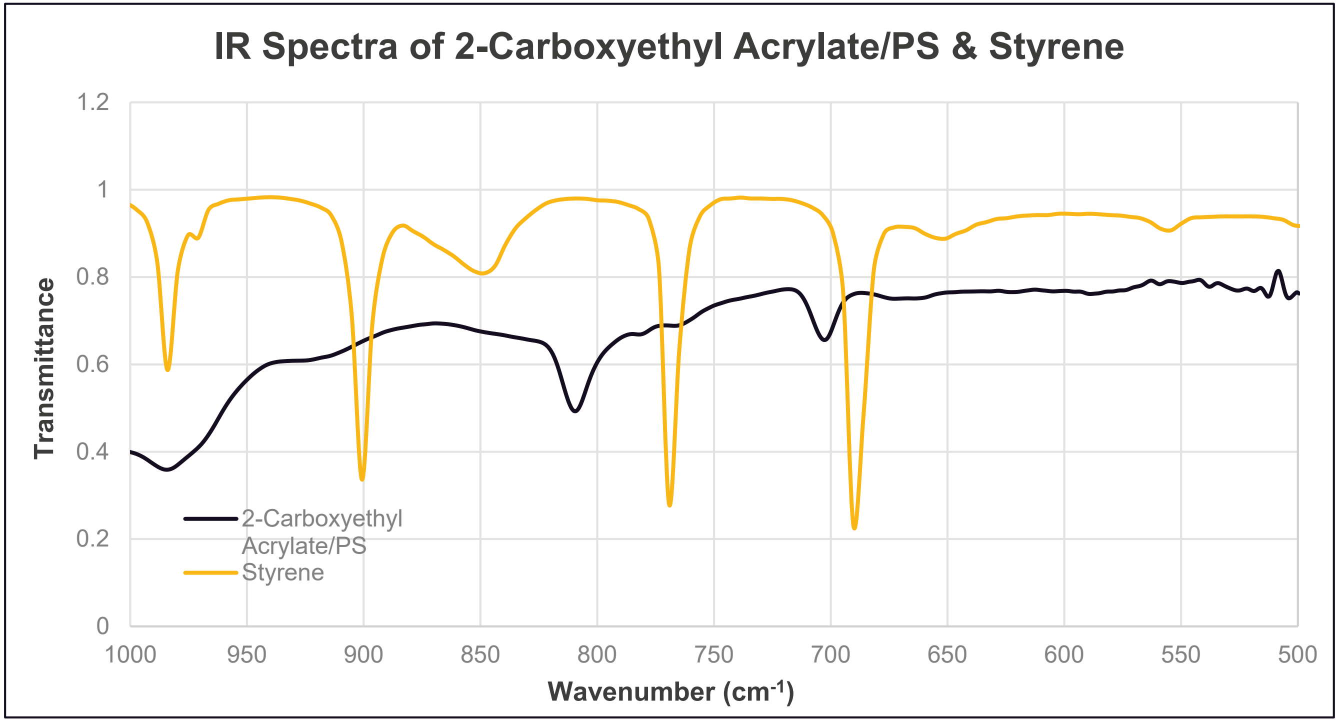

Fig. 17: *Zoomed-in insert of Fig. 15 from 500-1000 cm^{-1}. Styrene IR courtesy of www.webbook.nist.gov.*

Group	Range (cm^{-1})
R-CH=CH_2	985-1000 and 905-920
R_2CH=CH_2	880-900

Table 1: *IR frequency ranges (cm^{-1}) for functional groups relevant to styrene.*

Conclusions & Future Work

- Inconclusive polymerization trials
  - IR data suggests a lack of polymerization
  - Extended exposure to visible light resulted in solid composite
  - Vinyl toluene and styrene performed identically

- Future Work
  - Cationic photopolymerization
  - Incorporate gQDs to mitigate self-attenuation
    - UV-VIS Spectrophotometry
    - Fluorimetry
  - Stronger UV exposure to aid photopolymerization

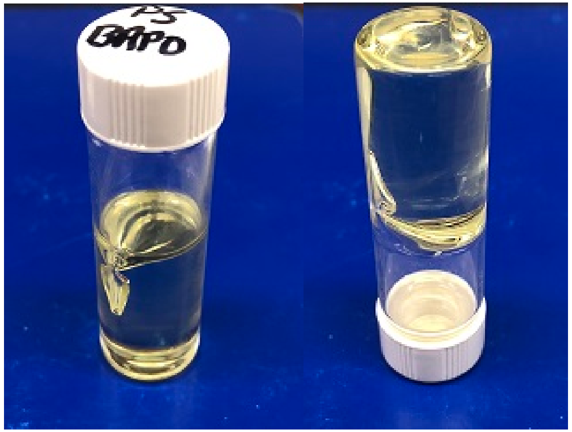

Fig. 18: *Solid styrene/BAPO composite after seven days of visible light exposure.*

Acknowledgements

- Special Thanks To…
  - Dr. Amanda Graff
  - Dr. Morag Smith
  - NEN-3: International Threat Reduction
  - NEN-1: Safeguards Science & Technology
  - MST-7: Engineered Materials
  - Workforce Development for Teachers and Scientists (WDTS)
  - Science Undergraduate Laboratory Internships (SULI) Program
  - Los Alamos National Laboratory (LANL)

Questions?

References

[1]Hajagos, T. J., Liu, C., Cherepy, N. J., Pei, Q., *Adv. Mater.* **2018**, 30, 1706956.

[2]Chao Liu, Zhou Li, Tibor Jacob Hajagos, David Kishpaugh, Dustin Yuan Chen, and Qibing Pei. *ACS Nano* **2017** *11* (6), 6422-6430

[3]Cherepy, N. J.; Sanner, R. D.; Beck, P. R.; Swanberb, E. L.; Tillotson, T. M.; Payne, S. A.; Hurlbut, C. R. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2015,** *778,* 126.

[4]Yanagida, T. Inorganic scintillating materials and scintillation detectors. *Proc. Jpn. Acad., Ser. B* **2018**, *94, (2), 75-97.*

[5]Hollingsworth, J. A. *Encycl. Inorg. Bioinorg. Chem.* **2011**, 1.

[6]Zhao, H.; Rosei, F. *Chem* **2017,** *3,* 229.

[7]Torchynska, T., Vorobiev, Y. Semiconductor II-VI Quantum Dots with Interface States and their Biomedical Applications. *Adv. Bio. Eng*. **2011.**

[8]Murphy, C. J., & Coffer, J. L. (**2002**). Quantum Dots: A Primer. *Applied Spectroscopy*, *56*(1), 16A-27A.

[9]S. E. Létant* and T.-F. Wang. *Nano Letters* **2006** *6* (12), 2877-2880

[10]Yagnaseni Ghosh, Benjamin D. Mangum, Joanna L. Casson, Darrick J. Williams, Han Htoon, and Jennifer A. Hollingsworth. *Journal of the American Chemical Society* **2012** *134* (23), 9634-9643